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Structure-dependence of the atomic-scale mechanisms of Pt electrooxidation and dissolution

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Abstract

Platinum dissolution and restructuring due to surface oxidation are primary degradation mechanisms that limit the lifetime of Pt-based electrocatalysts for electrochemical energy conversion. Here, we studied well-defined Pt(100) and Pt(111) electrode surfaces by in situ high-energy surface X-ray diffraction, on-line inductively coupled plasma mass spectrometry, and density functional theory calculations, to elucidate the atomic-scale mechanisms of these processes. The locations of the extracted Pt atoms after Pt(100) oxidation reveal distinct differences from the Pt(111) case, which explains the different surface stability. The evolution of a specific stripe oxide structure on Pt(100) produces unstable surface atoms which are prone to dissolution and restructuring, leading to one order of magnitude higher dissolution rates.

Introduction

The degradation of Pt catalysts for the cathode reaction in fuel cells is linked to their electrooxidation and dissolution.[1] Both these processes are arguably even more complex than the actual energy conversion via oxygen reduction and have been studied for a long time, mainly on polycrystalline and supported nanoparticle catalysts. Single-crystal studies offer the prospect of a more detailed understanding of these processes at the atomic level.[2–11] Some such studies followed these processes with potential cycling, where it is known that the surface restructuring over many cycles leads to a roughened surface, and that dissolution is enhanced during oxide reduction.[12–22] Explanation of this behaviour generally invokes a place exchange (PE) process, in which a Pt surface atom leaves its lattice site and oxygen penetrates into the metal lattice. On Pt(111), pioneering studies demonstrated that PE can be directly observed by surface X-ray diffraction (SXRD).[4,5] More recent SXRD measurements confirmed this[18,23–25] and allowed structural refinement, showing that the exchanged Pt atom lies 2.4 Å above its original lattice site,[18] in good agreement with density functional theory (DFT) studies of this process.[26–28] In contrast to Pt(111), other Pt crystal faces show distinct differences in the oxidation and dissolution behaviour.[10,12,14,29] This has been qualitatively explained by the more open arrangement of the surface atoms, but precise atomic level data are scarce. Thus, clear structure-reactivity relationships, which e.g. would guide the development of tailored Pt catalysts, are still lacking.

We here present detailed structural studies, focussing on the precise atomic motions in these early stages of oxidation. By correlating *in situ* SXRD measurements, which reveal how the place-exchanged Pt atoms are arranged in the initial stages of surface oxidation, with detailed DFT studies of this process, a direct comparison of the elementary processes underlying Pt(111) and Pt(100) oxidation becomes possible. Our study reveals a sharply different mechanism for the oxidative extraction of Pt atoms out of the two surfaces, providing a detailed explanation for the enhanced dissolution on Pt(100), observed by on-line mass spectroscopy.

Results

Dissolution and surface restructuring by electrooxidation.

According to cyclic voltammetry (CV) studies, the onset of Pt oxidation is marked on these two surfaces by a current peak above 1.0 V (labelled O_{ads} in Fig. 1b, c and Extended Data Fig. 1). However, the CV of Pt(100) irreversibly changes in subsequent cycles, whereas that of Pt(111) remains stable for an upper potential limit (UPL) of $\lessapprox 1.15$ V and thus can be mistaken for an oxidation process without surface restructuring.[7,12,29]

The (ir)reversibility of the CVs is mirrored in the Pt dissolution rates obtained by inductively coupled plasma mass spectrometry (ICP-MS) in a (capillary) scanning flow cell (CSFC and SFC) with results summarised in Fig. 1a,d. The facet dependent trends are readily apparent. At sweep rates of $\gtrapprox 10$ mV/s, no dissolution is seen for either surface for CVs with an UPL of 1.0 V, in agreement with previous results.[14,16] When increasing the UPL, the onset of significant anodic dissolution due to Pt oxidation is observed for Pt(100) as soon as the O_{ads} peak begins, while for Pt(111) the onset only occurs at potentials above 1.2 V. Cathodic dissolution during the oxide reduction is observed for both surfaces at UPLs ≥ 1.1 V; however, the dissolution of Pt(100) exceeds that of Pt(111) by about one order of magnitude. The onset and amount of dissolution depends on the precise time-potential program, reflecting the slow oxidation kinetics,[14] but the enhanced rates for Pt(100) as compared to Pt(111) are found in all experiments. It is noted that the amount of oxide formed in both cases is comparable, only about 20% higher for Pt(100) (as seen from the integral of the oxidation peaks in the CVs). Thus, the significant difference in dissolution rates points towards a fundamentally different oxidation behaviour of the two surfaces. Similar facet dependent trends have been found in previous comparative studies of the dissolution behaviour of Pt(100) and Pt(111),[14,16] but these do not link the difference to the oxide structure and also do not provide mechanistic explanations, due to the lack of knowledge on the structural changes during surface oxidation.

The atomic scale origin of this difference was investigated by *in situ* surface X-ray diffraction (SXRD). This technique determines the exact positions of surface atoms during the initial stages of oxidation, which can then be linked to the dissolution and surface restructuring mechanisms. For a qualitative assessment of the influence of surface orientation, we first followed reflections near the anti-Bragg positions of the crystal truncation rods (CTRs). Those are sensitive to the distortion of the ideal Pt lattice and the extraction of Pt atoms out of the surface in the place exchange process.[4,5,23] Performing such measurements during potential cycles revealed that on both surfaces the onset of PE coincides with the O_{ads} peak maximum (0.98 V and 1.04 V on Pt(100) and Pt(111), respectively), but that the subsequent structural response is very different (Fig. 1b,c). PE on Pt(100) results in irreversible surface structural changes, as indicated by the irreversible decrease in X-ray intensity after completion of one potential cycle. In contrast, the PE process on Pt(111) is initially fully reversible[4,23]

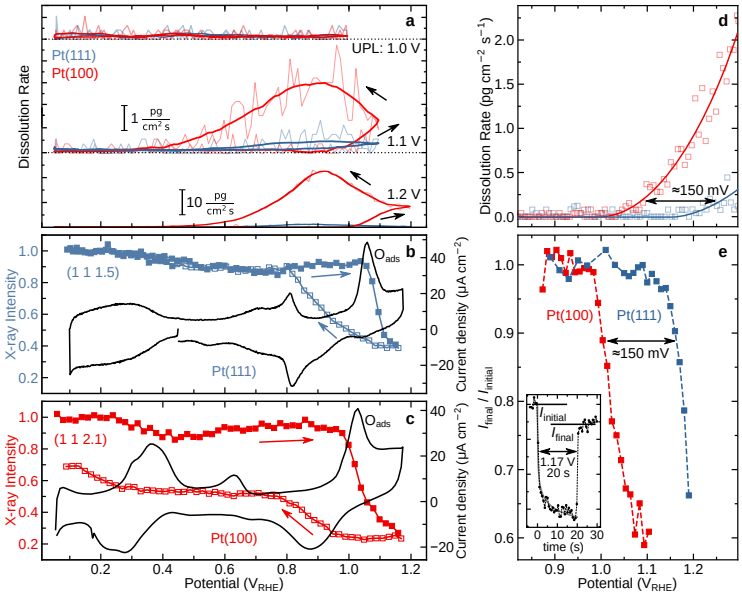

Fig. 1. Dissolution and atomic-scale structural changes during Pt oxidation. **(a)** Pt dissolution during cycles at 50 mV/s to increasingly positive potential limits (UPL) obtained using the capillary scanning flow cell, illustrating that the cathodic dissolution during oxide reduction is significantly more pronounced on Pt(100). X-ray intensity changes at the anti-Bragg positions of selected crystal truncation rods and simultaneously measured cyclic voltammograms of **(b)** Pt(111) (data taken from Ref. 23) and **(c)** Pt(100) during potential cycles at 20 mV/s. Pt place exchange (PE), indicated by the intensity drop at the O_{ads} peak, is initially fully reversible on Pt(111), whereas for Pt(100) it always results in irreversible surface restructuring. **(d)** Potential-dependent Pt dissolution rates during a positive sweep at 10 mV/s obtained with the scanning flow cell, showing the onset of anodic dissolution. **(e)** Reversibility of the PE process, determined by potential step experiments, where the potential was changed for 20 s from 0.47 V in the double layer range to a potential in the oxidation regime and then moved back to 0.47 V (illustrated in inset). The relative changes in X-ray intensity indicate that irreversible Pt surface restructuring starts at ≈ 150 mV higher potentials on Pt(111) than on Pt(100).

and only results in irreversible surface restructuring if the upper potential limit exceeds 1.15 V. Here, the onset of irreversibility occurs above a critical coverage of extracted Pt atoms,[23] which depends on potential and time in the oxidation regime. A more quantitative comparison of the onset of irreversible intensity changes, obtained in potential step experiments (Fig. 1e), indicates that these occur on Pt(111) at about 150 mV more positive potentials than on Pt(100), closely mirroring the onset of Pt dissolution (Fig. 1d). This unambiguously demonstrates that on single crystal surfaces dissolution and irreversible surface structural changes are linked.

Although the latter was already stated in the work of Lopes et al.,[14,15] here the dissolution behaviour was attributed to irreversible Pt oxide formation at the peak around 1 V, where on Pt(111) oxidation is still largely reversible. Furthermore, our observations resemble the *in situ* Raman spectroscopy data by Huang et al.,[10] who reported that bands associated with the formation of 3D α-PtO_2 oxide phase occur at 200 mV more negative potentials on Pt(100) than on Pt(111). However, PE on Pt(111) was here proposed to occur only at $\geq$ 1.3 V, which is at variance with the SXRD results. Therefore, a clear correlation between the precise oxide structure of different Pt surfaces, its reversibility, and its effect on the dissolution is still lacking.

Atomic-scale structure of the Pt oxide.

To assess the difference between the reversible and irreversible structural processes, we performed a detailed potential-dependent surface crystallographic analysis of an extended set of CTRs. An overview of all measured data sets is given in Supplementary Note 1. For Pt(111) the surface atom arrangement was determined in our previous study.[18,23] At low coverage, the PE was found to result only in an $\approx$ 2 Å vertical displacement of the extracted Pt atom (Pt_{ex}), whereas the in-plane position remains the same. The Pt_{ex} thus is located directly above its original site, which is now vacated or filled with oxygen. Previous density functional theory (DFT) studies also found this unusual geometry and indicated that it is stabilised by three neighbouring oxygen adsorbates on the Pt(111) surface.[27]

Similar structural characterisation of the initial stages of Pt(100) oxidation is more difficult, because unlike on Pt(111), the surface oxide continuously evolves over time scales of hours. This strongly impedes conventional SXRD measurements, which typically require 1 - 2 h recording time. We therefore performed *in situ* measurements by the novel technique of high-energy surface X-ray diffraction (HESXRD),[30] which allows collection of many CTRs in just a few minutes, i.e. in a time period over which the structural changes in the oxide are negligible. Examples of the CTRs measured on Pt(100) are shown in Fig. 2a (see Extended Data Fig. 3 for the full data set). Measurements at 0.12 V (Extended Data Fig. 2 and Supplementary Figure 2) confirm that the initial surface is unreconstructed and exhibits negligible roughness. At potentials slightly negative of the O_{ads} peak in the CV, adsorption of oxygen species is signalled by changes in the Pt surface relaxation and increased statistical deviations of Pt

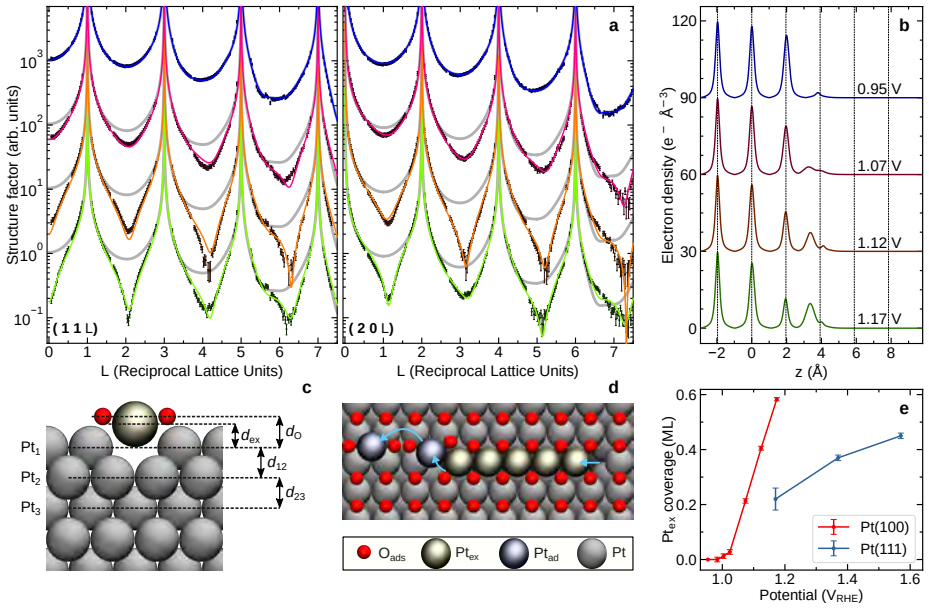

Fig. 2. Atomic structure of the place exchange site on Pt(100). **(a)** Two of the 11 measured crystal truncation rods (CTR) of Pt(100), obtained by *in situ* high energy surface x-ray diffraction measurements (68 keV) at a potential slightly negative (0.95 V) and three potentials positive (1.07, 1.12 and 1.17 V) of the O_{ads} peak in the cyclic voltammogram (Fig. 1b, Extended Data Fig. 1). The latter exhibit significantly decreased intensities and correspond to surfaces in which 20 to 60 % of the Pt atoms underwent place exchange. Each set of CTRs was recorded within 550 s, starting 300 s after the potential was established. The full CTR sets are given in Extended Data Fig. 3. In addition to the experimental data, which are offset by a factor of 10 with respect to each other, the best fit (coloured lines) and the CTR fits for the smooth surface at 0.95 V (grey line) are shown. **(b)** Electron density profile along the surface normal, obtained from the quantitative modelling of the CTRs. The bulk Pt lattice positions are indicated by dashed vertical lines. **(c)** Side and **(d)** top view of the atomic arrangement of the extracted Pt atoms (the labels correspond to the parameters in Supplementary Table 2). **(e)** Potential-dependent Pt_{ex} coverage on Pt(100), obtained from the crystal truncation rod analysis, compared with the Pt_{ex} coverage on Pt(111) (taken from Ref. 18).

surface atoms from ideal lattice positions, characterised by larger Debye-Waller factors. After the onset of PE, the intensity of all CTRs substantially decreases. This change cannot be described by Pt_{ex} in an on-top geometry, as in the case of Pt(111), or in conventional hollow or bridge sites atop the Pt surface. (see Supplementary Note 3 for details on the data analysis). A good description of the large HESXRD data sets was only possible by models that assume that the majority of extracted Pt atoms reside in bridge sites with vertical positions that are merely 1.40 Å (d_{ex} in Fig. 2c) above the Pt(100) surface plane (Fig. 2b). These models allowed fitting all of the CTR data obtained at different oxidation potentials, with very similar structure parameters, apart from the Pt_{ex} coverage, which continuously increased up to 0.6 ML with increasing potential (Fig. 2e, see Supplementary Table 2 for all structural parameters). It is noted that on Pt(111) the Pt_{ex} coverage increases more moderately, to 0.45 ML at 1.57 V.[18] The low vertical position of the Pt_{ex} is sterically incompatible with species residing atop the surface, but can be readily explained by Pt atoms that are bound via surface or subsurface oxygen to the centre of a vacancy dimer. The resulting geometry distinctly differs from that of Pt_{ex} on Pt(111), both in terms of the coordination as well as the distances of the Pt_{ex} to the neighbouring atoms in the Pt surface layer (about 0.2 Å larger) and the vertical spacing of the Pt_{ex} atoms from the layer below (d_{ex} >2.23 Å[18] on Pt(111), d_{ex} <1.42 Å on Pt(100)). Formation of such a vacancy dimer requires extraction of a second Pt atom from the surface layer (Pt_{ad}), which can be positioned as an adatom on the neighbouring Pt surface or as a slightly more protruded atom on the end of the dimer. However, Pt_{ex} and Pt_{ad} are not necessarily generated in equal numbers. For example, only one additional Pt_{ad} would be produced in the growth of a Pt oxide chain structure (Fig. 2d), similar to those found in scanning tunneling microscopy studies[31,32] and density functional theory (DFT) calculations[26] of Pt(111) oxidation in the gas-phase. In this case, the Pt_{ad} would only be formed as a minority species, not necessarily detectable in SXRD experiments. Indirect support for this scenario comes from CTR data obtained at 0.12 V after oxide reduction, which is shown in Extended Data Fig. 2. Here, Pt_{ad} in hollow sites are clearly present, but at coverages that are ten times lower than that of the Pt_{ex} in the corresponding oxide film. This suggests that also on Pt(100) the majority of Pt_{ex} directly return into surface vacancies after reduction.

Mechanism of oxide formation and Pt dissolution.

To further confirm the proposed structural development, we performed a comparative DFT study of the PE and Pt dissolution processes. We first calculated the Pourbaix diagrams for Pt(111) and Pt(100) (Extended Data Fig. 5) to determine the most stable oxygen coverage and adsorption sites as a function of pH and applied potential. The stabilization granted by water wetting was taken into account in the free energy assessment of all species (see the Methods section for further details).

In good agreement with the experimental data (Fig. 1b,c), platinum extraction is calculated to be thermodynamically favourable starting from 1.06 V at θ_O

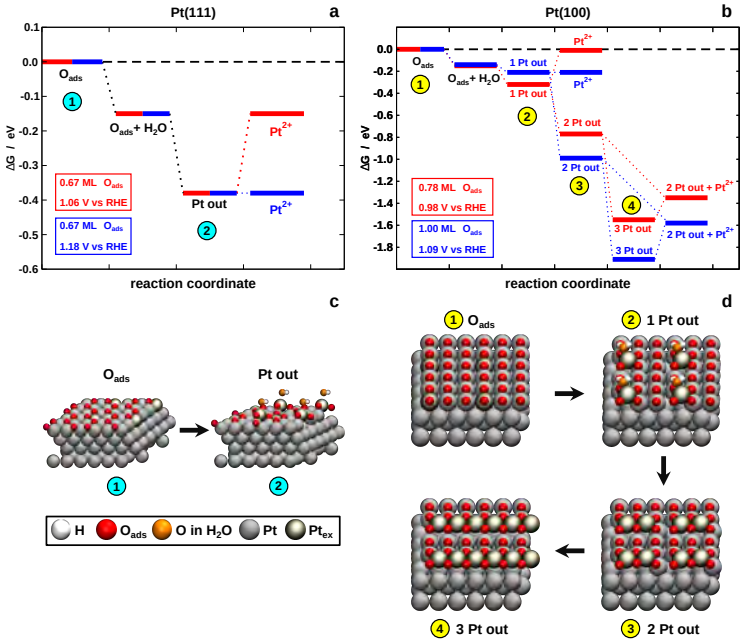

Fig. 3. Atomistic view of place exchange and dissolution on Pt(111) and Pt(100). Free energy landscapes of place exchange and dissolution obtained by density functional theory calculations of **(a)** Pt(111) and **(b)** Pt(100). Corresponding schematics of the main steps in the reaction pathway are shown in **(c)** and **(d)** for Pt(111) and Pt(100), respectively. In both cases, surface wetting by H_2O is accounted for and observed to aid the extraction process (for clarity, H_2O is not shown in step (3) and (4) of **(d)**). Dissolution of the first Pt_{ex} in form of Pt^{2+} is not favoured at low potentials (1.06 V on Pt(111), 0.98 V on Pt(100)), but becomes energetically favourable at higher potentials (1.18 V on Pt(111), 1.09 V on Pt(100)). Further Pt extraction proceeds differently on Pt(100), where a second and third extraction is favourable, leading to an extended extracted stripe of Pt atoms. Parallel to the stripe extraction process, dissolution can already occur at 0.98 V through detachment of one of Pt atoms in the dimer formed after the second stripe extraction. Top and side views of the surfaces are provided in Extended Data Fig. 6.

≈ 0.67 ML on Pt(111) and ≥ 0.98 V at $\theta_O \approx 0.78$ ML for Pt(100) (Extended Data Fig. 4). According to energy calculations of the various steps in the PE process (Fig. 3a,b), PE starts on Pt(111) with O_{ads} adsorption (Fig. 3, step (1)) followed by the extraction of a Pt atom (step (2)). In line with previous SXRD[18,23] and DFT[27] studies, the extracted Pt atom is located above a vacancy, and is coordinated to three O_{ads} atoms (Fig. 3c, Extended Data Fig. 6). Our extraction pathway on Pt(111) is similar to the one reported by Eslamibidgoli and Eikerling,[27] who found that PE starts at oxygen coverages between 0.59 and 0.75 ML. The pathway for PE on Pt(100) is substantially different from that on Pt(111) (Fig. 3b). Although it also starts by O_{ads} adsorption and the extraction of a Pt atom, the high O_{ads} coverage allows Pt extraction to immediately proceed at neighbouring sites. Hence, there is a consecutive extraction of Pt atoms that ultimately leads to the creation of a stripe of protruded atoms. In agreement with our experiments, the Pt_{ex} are not located above their original lattice sites but move sideways to a square-planar site where they are coordinated to four O_{ads} atoms. Because of the latter, this arrangement is strongly stabilised, contrary to Pt(111), where stripe-like structures only lead to small gains in free energy as compared to isolated Pt_{ex}.[26] The larger O_{ads} coordination around the Pt_{ex} may lead to the Raman signature resembling PtO_2, as observed for Pt(100) in this potential range.[10] Furthermore, we note that the first Pt_{ex} of each stripe has to deviate from the perfect square-planar site for steric reasons (see Pt_{ex} positions after first and second extraction), resulting in the more weakly bound Pt_{ad} species postulated above.

The differences in Pt(111) and Pt(100) anodic dissolution upon oxidation, i.e. the conversion of Pt_{ex} to a Pt ion (assumed to be Pt^{2+}),[33] can be ascribed to the different Pt extraction process. On Pt(111), the Pt_{ex} are initially arranged directly above the vacancy and this is thermodynamically more stable than a Pt^{2+}-vacancy pair (Fig. 3a and note in the Methods section). Only after the potential increases to 1.18 V does the dissolution become energetically favourable (Fig. 3a and Extended Data Fig. 4). The situation is different on Pt(100) (Fig. 3b), where the dissolution is not favoured at 0.98 V during the first extraction, but the atomic arrangement formed after the second extraction is prone to dissolution. DFT calculations show this process to be exothermic and to result in the same structure after removal of a Pt_{ex} atom from the second and third extraction state. The reason for this is that in the case of dissolution from the second extraction state subsequent extraction of a further Pt surface atom occurs. This leads to stabilization of the system, because the formed dimer is now better positioned in the triple vacancy. Thus, the Pt_{ex} atoms formed in the initial stages of stripe formation as well as the more weakly bound Pt_{ad} at the ends of stripes are prone to dissolution. This explains the higher anodic dissolution rates and lower dissolution potentials of Pt(100) as compared to Pt(111), where no similar destabilised atoms exist. After the potential exceeds that for 1 ML O_{ads} coverage (1.09 V), the dissolution can also take place during the first extraction step.

The initial reversibility of PE and stability against cathodic dissolution on Pt(111) can be attributed to the on-top arrangement found in our SXRD and

DFT studies, when the Pt_{ex} coverage is low and the Pt(111) lattice around the vacancy on which the O_{ads} atoms are adsorbed remains intact. This on-top geometry facilitates back insertion of the Pt_{ex} into the vacancy after desorption of oxygen in the reduction process (ΔG_{ex} = -0.5 eV at θ_O = 0.44 ML, Extended Data Fig. 4) rather than formation of a Pt adatom - vacancy pair via detachment or dissolution in the form of Pt^{2+} as discussed in Ref. 15. At higher Pt_{ex} coverage the oxide surface structure is more complex, impeding straightforward conclusions on the exact restructuring process. However, the increasing deviations of the Pt_{ex} from the on-top positions, observed by SXRD,[18] suggest a gradual loss of the overall integrity of the Pt surface lattice, which may account for the irreversible surface roughening during subsequent oxide reduction as well as for Pt cathodic dissolution.

In contrast, on Pt(100) we expect Pt adatoms and Pt^{2+} formation directly from the ends of the Pt_{ex} stripes during oxide reduction. Similarly, adatoms and Pt^{2+} are also expected to form during the oxide reduction, i.e. upon a decrease in the O_{ads} coverage. While the stripes are shortened, the remaining destabilised Pt_{ad} at the end of the stripe are more likely to dissolve or form adatoms.

Conclusion

In conclusion, the onset potentials of anodic dissolution on Pt(100) and Pt(111) correspond to the onset of irreversibility in the extraction of the first Pt atoms from their lattice sites as the surface is oxidized. According to our combined SXRD and DFT studies, the marked difference in behaviour of the two surfaces has its origin in the different atomic structures of the initial oxide. On Pt(111), the extracted Pt atom lies directly above its original site, and reversibility for low coverages is explained by its facile return to that site. However, on Pt(100) the extracted Pt atom moves laterally away from its original site and initiates immediate extraction of a second atom, leading to the formation of a stripe structure. This mechanism produces unstable surface atoms at the stripe ends, which can be dissolved both during the oxidation itself and during subsequent oxide reduction, making the process irreversible from its onset.

As shown by our data, the precise Pt extraction mechanisms during oxidation and the accompanying dissolution differ substantially on different Pt facets. This sensitivity of Pt electrocatalyst degradation on surface structure has to be taken into account in the quest for a knowledge-based approach, where highly stable catalysts are ideally predicted *ab initio*. While our study represents the first step in developing an atomistic picture of these processes for surfaces other than Pt(111) (which may be considered as an atypical case according to the results presented here), further studies are necessary, especially of more open high-index surfaces. Such detailed insight into the degradation mechanisms of structurally defined model systems is an important prerequisite for the challenging task of *ab initio* modelling the stability of real catalyst particles and, ultimately, developing rational strategies for the design of catalysts with improved stability.

Methods

Sample preparation.

All experiments employed cylindrical Pt single crystals (Mateck, Crystal Preparation Laboratory) and Ar-purged 0.1 M $HClO_4$ solution made from ultrapure water and suprapur® perchloric acid (Merck). Potentials were measured versus Ag/AgCl ($KCl_{sat.}$, SFC-ICP-MS or 3.4 M KCl, SXRD) reference electrodes but are reported against the reversible hydrogen electrode (RHE). The Pt crystals were initially cleaned in an ultra-high vacuum chamber using repeated Ar^+-ion bombardment and subsequent annealing at 900 °C in 10^{-6} mbar oxygen. Prior to each experiment, the Pt crystals were prepared by flame annealing with a butane torch (SFC-ICP-MS) or by annealing under 2 % CO/ 98 % Ar in an induction oven (Himmelwerk HU-2000+, SXRD). Subsequently, the sample was cooled in a flow of Ar/H_2 (SFC-ICP-MS) or 2 % CO/ 98 % Ar (SXRD) and transferred to the cell protected either by a drop of Ar saturated ultrapure water or the adsorbed CO layer (SXRD, only Pt(100)). Immersion into the electrolyte was performed under potential control at potentials in the double layer regime. After immersion, remaining adsorbed CO was removed by anodic stripping.

Dissolution measurements.

The dissolution measurements at low scan rate of 10 $mV \cdot s^{-1}$ to resolve the onset potentials of dissolution were conducted using the classical scanning flow cell coupled to an inductively coupled plasma mass spectrometer technique (referred to as SFC-ICP-MS, NexION 300X, Perkin Elmer). The working electrode (WE) had a contact area of 0.035 cm^2. The flow rate of the SFC-ICP-MS was ca. 170 $\mu L \cdot min^{-1}$. ^{187}Re was used as an ICP-MS internal standard for platinum. A graphite rod was used as a counter electrode and a double junction Ag/AgCl (Metrohm) as a reference electrode. Details on the SFC-ICP-MS measurements are given in Ref. 34, 35. The CV experiments at relatively fast scan rates were carried out using a modification to the SFC-ICP-MS, referred to here as the CSFC-ICP-MS (capillary SFC-ICP-MS), which allows for significantly increased time-potential resolution.[36] By inserting a small capillary directly above the working electrode (Supplementary Figure 9) and connecting directly to the ICP-MS via self-aspiration (bypassing the use of the peristaltic pump) delay times between the dissolution on the WE and ICP-MS detection can be reduced from ca. 25 to 3 s. Reduced delay times and shorter tubing distances limit the dispersion of dissolved species, and therefore enhance the resolution of dissolution rate profiles, e.g. to clearly separate anodic and cathodic dissolution signals.[37] The relatively fast flow rate of 580 $\mu L \cdot min^{-1}$ resulted in a collection efficiency >99 %. Further details on this new technique can be found in Ref. 38.

Electrochemical cell for surface x-ray diffraction.

All Surface X-ray Diffraction (SXRD) experiments employed the established SXRD electrochemical cell, described in Ref. 39. Inside this cell, the upward facing single-crystalline surface of the crystal sample is in contact with the electrolyte via a free-standing meniscus. This geometry is similar to the hanging meniscus geometry commonly used in single crystal electrochemistry and minimises contributions from the defect-rich edges of the crystal. The amount of electrolyte inside the cell was controlled remotely using a motorised pump system with a precision of 1 µl. To prevent oxygen contamination, the meniscus was kept in Ar atmosphere and the electrolyte reservoirs were continuously purged with Ar. We used a high-purity Pt foil with a surface area of about 120 mm^2 as counter electrode and a Ag/AgCl (3.4 M KCl, eDaq) reference electrode. The reference electrode was connected by a micron-sized hole to a glass capillary, which was filled with 0.1 M $HClO_4$ and served as Luggin capillary and salt bridge. This arrangement effectively ensured negligible leakage of KCl from the reference electrode to the cell. The cell and all glassware and tubing that were in contact with the electrolyte had been previously cleaned by soaking in a 4:1 mixture of concentrated H_2SO_4 and 30 % H_2O_2 for at least 1 day. Afterwards, all materials were rinsed and boiled repeatedly in high-purity water (Elga purelab ultra 18.2 MΩ cm). Cyclic voltammograms (CVs) of Pt(111) and Pt(100) in 0.1 M $HClO_4$ in the double layer potential region, prepared in this way and measured in the SXRD electrochemical cell, are shown in Extended Data Figure 1. For both surfaces, the voltammograms are in good agreement with those reported in the literature.[29] CVs up to 0.6 V were recorded at the beginning of every SXRD experiment to check that a high surface quality had been obtained by the annealing process.

Surface x-ray diffraction setup.

All SXRD experiments were performed at undulator beamlines ID03 and ID31 of the European Synchrotron Radiation Facility using a six-circle geometry and constant incident angle. A schematic illustration of the experimental setup is shown in Supplementary Figure 6. The crystal inside the SXRD cell was positioned with the surface facing upwards. Conventional SXRD studies were performed at beamline ID03 and focused on kinetic studies of the Pt oxidation process by measuring the X-ray intensity at a fixed position along a crystal truncation rod (CTR). Similar as in our previous studies,[17,18,23,24,40] these measurements employed a photon energy of 22.5 keV, a (vert./hor.) beam size of 45×750 $µm^2$ and an angle of incidence of 0.3°. A small 2D detector (Maxipix) mounted on the diffractometer arm was used to simultaneously measure the crystal truncation rod (CTR) intensity and the background intensity with a time resolution of 0.1 s. The structure factor of the CTR at the studied reciprocal space position was determined by first subtracting the background intensity and then taking the square root of the integrated diffraction rod intensity.

Operando high-energy SXRD (HESXRD) measurements of the Pt(100) CTRs

were performed at the high-energy beamline ID31 at a photon energy of 68 keV. To enhance the surface contribution, the incident angle was kept at 0.05°, which is below the critical angle of total external reflection. The beam size at the sample position was 12×48 µm^2. The orientation of the surface normal direction was aligned better than 0.005° relative to the in-plane rotation axis, to ensure that the angle of incidence did not change during sample rotation. The diffracted X-ray intensity was recorded with a stationary, large-area X-ray detector (Pilatus 2M CdTe), which was positioned 73 cm behind the sample. This allowed covering a range of up to 12 Å^{-1} momentum transfer perpendicular to the surface and a range of about ±5.5 Å^{-1} momentum transfer parallel to the surface. The tilt angles between the detector plane and the incident beam direction were determined by recording the Debye-Scherrer rings of a CeO_2 powder calibration standard and analysing these data with the *pyFAI* software.[41] The calculations of the reciprocal space coordinates for each detector pixel were performed using the tilt-corrected angles. The position of all visible Bragg reflections on the detector and the corresponding observed sample rotations were used to accurately determine the orientation of the crystal as described in Ref. 42. After mounting and alignment of the Pt sample, the positions of the ≈ 30 Bragg reflections from the bulk crystal were masked using small W pieces, placed directly in front of the 2D detector. This is necessary to prevent damage to the detector by the intense Bragg reflections, while measuring the weak CTR intensities with the unattenuated incident beam. The beamstops manifest as black areas on the detector frames (see Supplementary Figure 8 and missing data points in the CTR profiles). In addition, the incident beam was blocked by a beamstop located about 10 cm behind the sample, to reduce air scattering background.

Points in reciprocal space were described in terms of the Miller indices (H K L), where H and K correspond to reciprocal lattice unit cell vectors $\vec{b_1}$ and $\vec{b_2}$ in the surface plane and L to a vector $\vec{b_3}$ along the surface normal. For Pt(100) we chose the conventional cubic reciprocal basis with lattice vectors $|\vec{b_1}| = |\vec{b_2}| = |\vec{b_3}| = 2\pi/a$ with $a = 3.9242$ Å being the Pt lattice constant. In the case of Pt(111) we used a hexagonal unit cell with reciprocal lattice vectors of length $|\vec{b_1}| = |\vec{b_2}| = 8\pi/\sqrt{6}a$ and $|\vec{b_3}| = 2\pi/\sqrt{3}a$, which is common in SXRD studies of fcc(111) surfaces.[43] A schematic illustration of the reciprocal space geometry of Pt(111) and Pt(100) is shown in Supplementary Figure 7. The Bragg reflections of Pt(111) are separated by $\Delta L_{\mathrm{Bragg}} = 3$ and the ones for Pt(001) are separated by $\Delta L_{\mathrm{Bragg}} = 2$ along the CTRs. The absence of some CTRs, such as (1 0 L), (2 1 L), etc. for Pt(100), is related to the chosen fcc unit cell.

Determination of the CTR structure factors.

Crystal truncation rod (CTR) data are commonly presented by plotting the structure factor F_{HKL} as a function of L. To determine these structure factors by HESXRD, the reciprocal space is mapped by continuously recording detector

frames during a single rotation of the crystal around the surface normal.[30] By summing up all the detector frames recorded during a reciprocal space mapping, the CTRs can be directly visualized (Supplementary Figure 8, vertical lines). Since the unit cell of Pt(100) has a rotational symmetry of 90°, a 110° rotation was sufficient to collect all symmetrically non-equivalent CTRs. An angular resolution of 0.05° was chosen to achieve high enough reciprocal space resolution at the low L values of the (3 1 L) CTR. From these data, the CTR structure factors were determined using the *binoculars* software.[44] Here, first correction factors for solid angle and polarisation are applied to the measured intensities.[45] Then, a 3D representation of the reciprocal space is calculated by binning the intensities of each individual pixel, using the reciprocal space coordinates on each frame. For the analysis of the Pt(100) data, bin sizes of $\Delta H = 0.002$, $\Delta K = 0.002$ and $\Delta L = 0.03$ were used. This corresponds to a series of HK-slices along the CTR, which are separated by the distance ΔL. Within this ΔL range, the structure factor F_{HKL} of the CTR is assumed to be constant and was determined by taking the square root of the integrated X-ray intensity at the CTR position. The background intensity was integrated in a region close to the CTR position and was subtracted from the CTR intensity. A more detailed description of the direct structure factor extraction in reciprocal space is given in the paper by Drnec et al.[46] To obtain the statistical uncertainties σ_2 of each reflection, we extended the *binoculars* software by a package that calculates these uncertainties according to Poisson statistics. The total number of measured reflections in each CTR dataset was between 1922 and 2005. After averaging of symmetry equivalent reflections, between 802 and 808 reflections were available for the structural analysis. The agreement factor ε of the symmetry equivalent reflections was 0.08 ± 0.07. The uncertainties of the averaged reflections were then calculated to $\sigma = \sqrt{\varepsilon^2 F_{HKL}^2 + \sigma_2^2}$.

Fitting of structural models to the CTR data.

To obtain the atomic positions of the surface atoms, all CTRs of a given data set were jointly fitted by a surface structural model using a Python-based software, developed by us for the quantitative analysis of HESXRD data. In this software, the structure factors, calculated from the model using kinematic scattering theory,[47] are fitted to the experimentally observed structure factors by the least squares method. A detailed description of the analysis of the CTRs in the double layer region and in the region of oxide formation is given in Supplementary Note 2 and 3, respectively. The statistical errors of the best-fit parameters given in Supplementary Tables 1-4 were calculated with the covariance matrix method.[48] These errors only take into account the goodness of fit and the experimental errors of the observed reflections, which are given by the counting statistics and the agreement factor between symmetry equivalent reflections. Systematic errors due to the chosen fit model are not included here. Those can be estimated from Supplementary Table 4, where for two central parameters, the occupancy and height of the Pt_{ex} atoms, and three characteristic potentials, 1.07 V, 1.12 V and 1.17 V, the results of the best fits obtained by

four different surface models are given.

Computational methods.

The density functional theory calculations were carried out using the VASP code, version 5.3.5-avx.[49] The PAW method[50] was used to describe the interaction between the core electrons and the valence electron density, described by means of a plane-wave basis set, and the PBE exchange-correlation functional.[51] In the optimization, we used a plane-wave cutoff of 450 eV, the convergence criterion for the atomic forces was $0.05\,\mathrm{eV}\cdot\mathrm{\AA}^{-1}$ and dipole corrections were applied between periodically repeated images in the z-axis. In the 4-layer-thick (3×3) Pt(111) and (3×3) Pt(100) slabs the two topmost layers and the adsorbates were fully relaxed, while the two bottommost layers were fixed. For both slabs the k-point sampling was (4×4×1). H_2 and H_2O were simulated in cubic boxes of $3375\,\mathrm{\AA}^3$, sampling the gamma point only. The free energies were approximated as: $G = E^{DFT} + ZPE - TS + G^{solv}$. The zero-point-energy (ZPE) and vibrational-entropy (TS^{vib}) corrections were calculated within the harmonic oscillator approximation for the adsorbed species, whereas for H_2 and H_2O the values were taken from thermodynamic tables (see Supplementary Tables 5 and 6).[52] Solvation contributions to the adsorption energies (G^{solv}) of H_2O_{ads} and OH_{ads} were taken from previous studies.[53,54] Proton-electron transfers were modelled with the computational hydrogen electrode.[55] The Pourbaix diagrams of Pt(111) and Pt(100) in Extended Data Fig. 5 were built following the methodology described in Ref. 56.

The energetics of Pt dissolution as Pt^{2+} and $PtOH^+$ was evaluated based on the experimental standard dissolution potential of Pt of 1.18 V and that of the reaction, which is 1.20 V.[52] From those two reactions, we conclude that Pt^{2+} is slightly favoured over $PtOH^+$, thermodynamically speaking. Besides, we note that the cohesive energy of bulk Pt provided by PBE is 5.54 eV, while in experiments it is 5.87 eV.[57] Thus, a correction of 0.33 eV needs to be applied.

In calculated Pourbaix diagrams (Extended Data Fig. 5), we observe that O_{ads} (i) is more strongly adsorbed on Pt(111) compared to Pt(100) at the same coverage and (ii) adsorbs at twofold bridge sites on Pt(100) and at threefold fcc hollow sites on Pt(111) (Supplementary Table 5). At a given potential, the oxygen coverage (θ_O) is typically larger on Pt(100) with respect to Pt(111), due to lower lateral repulsion, and corresponding well with previous calculations.[56,58]

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Author Contributions

All authors performed experimental work and were involved in the experiment design. T.F. and D.J.S.S. analysed SXRD and SFC-ICP-MS data respectively. F.C.-V. performed DFT calculations. T.F., J.D. and O.M.M. prepared the manuscript. All authors were involved in data interpretation and editing of the manuscript.

Competing Interests

The authors declare no competing interests.

Data availability

The raw X-ray data as well as the atomic coordinates of the optimized computational models have been deposited in the repository https://doi.org/10.5281/zenodo.3937672. All other data supporting the findings of this study are available within the article and its Supplementary Information, or from the corresponding author upon reasonable request.

Code availability

The custom software for the analysis of the CTR data and the custom *binoculars* backend for HESXRD structure factor determination are deposited in the repository https://doi.org/10.5281/zenodo.3941003. All other software used for this study is publicly available or can be obtained from the corresponding author upon reasonable request.

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Supplementary Information: Structure-dependence of the atomic-scale mechanisms of Pt electrooxidation and dissolution

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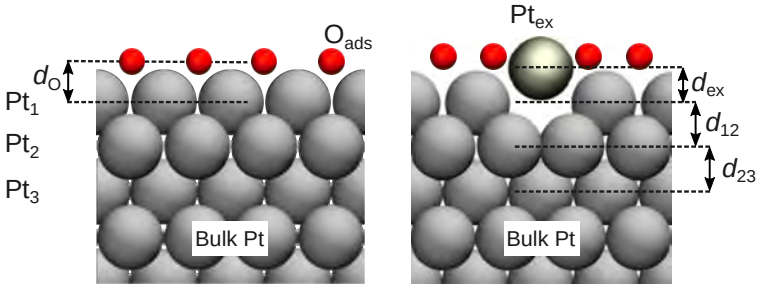
Supplementary Note 1: Overview of CTR measurements

CTR data sets of Pt(100) were obtained at two potentials in the double layer region, 0.12 and 0.95 V, and at the following 6 potentials in the Pt oxidation region: 0.984, 1.00, 1.02, 1.07, 1.12 and 1.17 V. At each potential 11 CTRs were measured up to L values of 7.5, of which the following are symmetrically equivalent:

- (1 1 L), (-1 -1 L)
- (0 2 L), (0 -2 L), (2 0 L)
- (2 2 L), (-2 -2 L)
- (1 3 L), (-1 -3 L), (3 1 L), (1 -3 L)

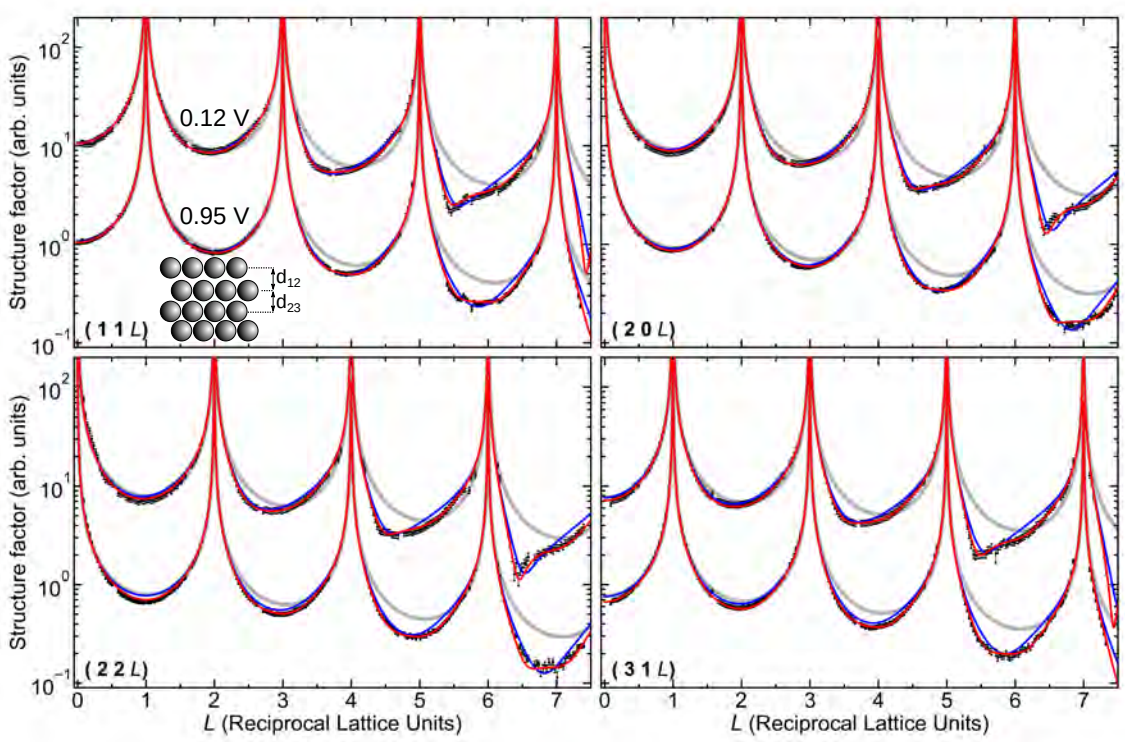
The full data for 4 different potentials are displayed in Extended Data Fig. 3. Coloured lines show the results of best fits by the models presented in Supplementary Figure 1, which are discussed in the following sections. The CTR data obtained at other potentials are in full accordance with the presented results.



Supplementary Figure 1. Schematic illustration of the models used for fitting of the CTR data of Pt(100) at **(a)**: 0.95 V and **(b)**: 1.07, 1.12 and 1.17 V. Free fit parameters were the interplanar distances d_{ex}, d_{12} and d_{23}, the coverage of the exchanged Pt_{ex} atoms θ_{ex} and the mean displacements Δr_i of the respective position of the atoms Pt_i, corresponding to the Debye-Waller factors. The in-plane component $(\Delta r_i)_{\parallel}$ and out-of-plane component $(\Delta r_i)_{\perp}$ of the mean atomic displacements have been fitted individually.

Supplementary Note 2: Initial surface quality and structure in the double layer region

The initial surface quality of the freshly prepared Pt(100) surface was characterised in the region of H adsorption and OH adsorption (0.12 V and 0.95 V). At those potentials only the CTRs were observed; additional in-plane peaks associated with a reconstructed surface were not found. The measured, as well as the calculated CTRs of a bulk-terminated crystal are shown in Supplementary Figure 2. At small L, the measured structure factor is close to the rod profile of a bulk-terminated crystal, indicating a surface with a very small defect density. However, with increasing L the curves gradually deviate from the rods of the bulk-terminated crystal. This can be attributed to higher vertical Debye-Waller factor of the surface atoms compared to the bulk Debye-Waller factor. A shift of the minima to lower L can be assigned to a lattice expansion of the top Pt layers. Overall, these effects are more pronounced in the region of H adsorption, which is in good agreement with Tidswell el at. who found a larger lattice expansion of the very first Pt layer in the region of H adsorption than in the region of OH adsorption.[1] For further quantitative analysis we used a model of an unreconstructed surface with either one or two expanded top Pt layers. Adsorbed hydrogen was not included in the model since the X-ray scattering from hydrogen is negligible at high energies. Water layering was also not included, because it does not contribute to the non-specular CTRs given its low in-plane order. Free fit parameters were d_{12} and d_{23} and the in-plane and out-of-plane Debye-Waller factors of the Pt_1 and Pt_2 layer. The bulk Debye-Waller factor has been fitted freely at the diffraction rod at 0.12 V. The corresponding fits using the two models, one layer and two layers relaxation, are shown in Supplementary Figure 2 and the best-fit parameters are given in Supplementary Table 1.



Supplementary Figure 2. CTRs of Pt(001) at 0.12 V in the region of H_{ads} and at 0.95 V in the region of OH_{ads} close to the onset of oxidation. The grey lines are the CTRs of a bulk terminated surface. Blue and red lines show CTR fits with vertical relaxations (d_{12}, d_{23}) of one or two Pt layers, respectively.

E_{RHE}	**0.95 V**		**0.12 V**	
Model	2 relaxed layers	1 relaxed layer	2 relaxed layers	1 relaxed layer
d_{12}/Å	1.9892 ± 0.0005	1.9893 ± 0.0005	2.0147 ± 0.0006	2.0175 ± 0.0005
d_{23}/Å	1.96948 ± 0.00024		1.97191 ± 0.00028	
$(\Delta r_1)_{\parallel}$/Å	0.1034 ± 0.0021	0.077 ± 0.004	0.0946 ± 0.0026	0.074 ± 0.004
$(\Delta r_2)_{\parallel}$/Å	0.0742 ± 0.0019		0.0785 ± 0.0022	
$(\Delta r_1)_{\perp}$/Å	0.1096 ± 0.0004	0.1054 ± 0.0005	0.1030 ± 0.0004	0.0972 ± 0.0007
$(\Delta r_2)_{\perp}$/Å	0.0844 ± 0.0004		0.0847 ± 0.0005	
χ_r^2	1.05	3.04	0.67	1.81

Supplementary Table 1. Structure parameters of the pristine surface at 0.12 V and 0.95 V obtained by fitting of the diffraction rods. Two models have been considered either with one expanded Pt layer or two expanded Pt layers. Errors are estimated from the diagonals of the covariance matrix.

As expected, the data at 0.12 V and 0.95 V can be described well with an unreconstructed surface. The fit with an increased interplanar distance d_{12} is already in good agreement with the data, but inclusion of a second expanded interplanar distance d_{23} does significantly improve the fit. Note that the differences in both models are only becoming apparent at very high L, which is not commonly measured in conventional SXRD, since it requires very long data aquisition times and is above the range of movement for most diffractometers.

After inclusion of 2 relaxed Pt layers, the fit matches the data within the experimental errors, with $\chi_r^2 = 1.05$ and $\chi_r^2 = 0.67$ for the data sets at 0.95 V and 0.12 V, respectively. Allowing additionally for surface roughness by reducing the coverage of the topmost Pt layer does not improve the fit in either of the models, indicating that the initial Pt surface is atomically smooth. The fit of the data set at 0.12 V yields an expansion of 2.68 % relative to the interplanar distance of the Pt bulk lattice (d = 1.9621 Å). This is higher than the value obtained in a similar experiment by Tidswell et al., who found an expansion of up to 1 %. However, the amount of surface defects was much higher than in our case, which may explain the difference. The best fit shown in Extended Data Fig. 2 is the CTR fit with 2 relaxed Pt layers.

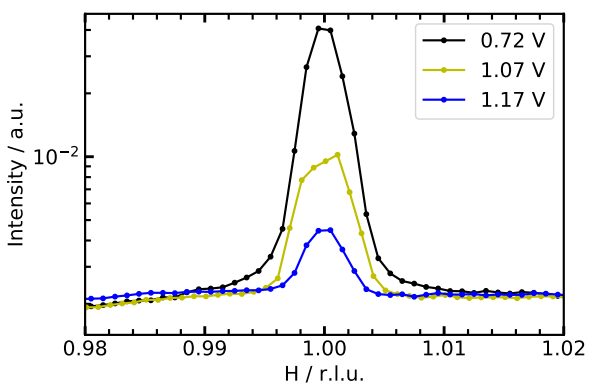
The adsorption of oxygen species at 0.95 V is indicated by a reduction of the Pt layer expansion to 1.38 %. However, inclusion of adsorbed oxygen species in the surface model has only a minor effect on the fit quality, independent of the chosen O_{ads} adsorption site (top, bridge, hollow), because its scattering contribution can be easily compensated by small changes in the Pt distances and Debye-Waller factors. Nevertheless, it is clear that oxygen is present on the surface at this potential. We therefore included an adsorbed oxygen monolayer in the fit of the data at 0.95 V

presented in Fig. 2, with the oxygen site and coverage being chosen according to the results of the DFT calculations. This results in $\chi_r^2 = 1.01$, i.e., a marginally better value as compared to the model without O_{ads}.

The Debye-Waller factor for the bulk Pt atoms, obtained in this final fit of the data at 0.12 V ($\Delta r_{bulk} = 0.0743\,\text{Å}$), was used as a fixed parameter in the subsequent analysis of the surface oxide.

Supplementary Note 3: CTR analysis of the Pt(100) oxide

The oxide studied in the CTR analysis was formed by linearly sweeping the potential by $50\,\mathrm{mV/s}$ to a given potential in the region of oxide formation, and subsequently holding the potential at this value for 5 min before starting data acquisition. This ensures that the oxide structure has reached a quasi-stationary state, in which residual slow changes in the oxide structure [2] are negligible over the time of the measurement. During the HESXRD measurement, the potential was kept constant. After the first measurement at 0.12 V, the potential was increased by a linear sweep and the measurement was repeated at the next potential after 5 min of holding time. This procedure was carried out for potentials 0.95 V, 0.98 V, 1.00 V, 1.02 V, 1.07 V, 1.12 V and 1.17 V. At none of these potentials additional diffraction peaks or rods associated with a well-ordered oxide were observed. Furthermore, no increase in background scattering due to diffuse scattering from the oxide can be observed, suggesting that this signal is too weak to be distinguishable from the liquid background scattering. The latter is illustrated in Supplementary Figure 3, where the intensity distribution along the H-direction at the (1 1 2) position is shown as an example.



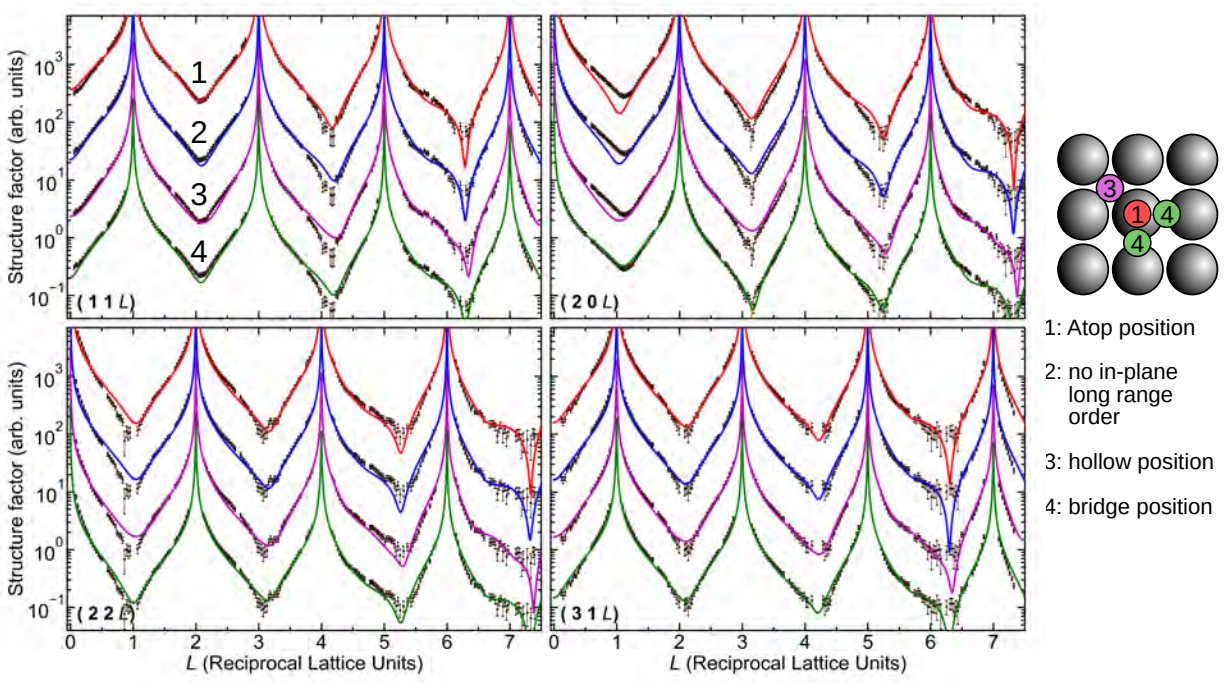
Supplementary Figure 3. Scattering along the H-direction at the (1 1 2) position of Pt(100) at different potentials in the oxidation region (1.07 V, 1.17 V) and prior oxidation at 0.72 V. No increase of background scattering adjacent to the CTR is observed. Note that these measurements were performed at a lower photon energy of 22.5 keV at ID03 to increase the reciprocal space resolution.

E_{RHE}	**1.17 V**	**1.12 V**	**1.07 V**	**0.95 V**
θ_{ex}/ML	0.583 ± 0.006	0.405 ± 0.007	0.213 ± 0.008	
d_{ex}/Å	1.407 ± 0.011	1.409 ± 0.014	1.29 ± 0.04	
d_{O}/Å	2.069 ± 0.020	2.15 ± 0.04	1.97 ± 0.08	1.797 ± 0.026
d_{12}/Å	1.9271 ± 0.0011	1.9436 ± 0.0011	1.9592 ± 0.0009	1.9889 ± 0.0005
d_{23}/Å	1.9794 ± 0.0005	1.9702 ± 0.0006	1.9692 ± 0.0005	1.96944 ± 0.00024
$(\Delta r_{\mathrm{ex}})_{\parallel}$/Å	0.493 ± 0.008	0.541 ± 0.018	0.35 ± 0.04	
$(\Delta r_{\mathrm{O}})_{\parallel}$/Å	0.30 ± 0.04	0.40 ± 0.06	0.21 ± 0.05	0.44 ± 0.04
$(\Delta r_{1})_{\parallel}$/Å	0.074 ± 0.014	0.091 ± 0.009	0.102 ± 0.006	0.1047 ± 0.0021
$(\Delta r_{2})_{\parallel}$/Å	0.079 ± 0.005	0.085 ± 0.004	0.074 ± 0.004	0.0742 ± 0.0019
$(\Delta r_{\mathrm{ex}})_{\perp}$/Å	0.202 ± 0.011	0.175 ± 0.021	0.258 ± 0.027	
$(\Delta r_{\mathrm{O}})_{\perp}$/Å	0.07 ± 0.05	0.07 ± 0.07	0.173 ± 0.027	0.08 ± 0.04
$(\Delta r_{1})_{\perp}$/Å	0.0858 ± 0.0026	0.0967 ± 0.0019	0.1112 ± 0.0009	0.1089 ± 0.0004
$(\Delta r_{2})_{\perp}$/Å	0.1011 ± 0.0010	0.0962 ± 0.0009	0.0922 ± 0.0007	0.0843 ± 0.0004
χ^2_r	3.182	3.21	1.977	1.013

Supplementary Table 2. Structural parameters of the potential dependent oxide structure of Pt(100) in steady-state obtained from a fit of the CTRs in Fig. 2 and Extended Data Fig. 3. Errors are estimated from the diagonals of the covariance matrix.

The CTRs obtained at 0.95, 1.07, 1.12 and 1.17 V are displayed in Fig. 2 and Extended Data Fig. 3. The CTRs at 0.98 V, 1.00 V and 1.02 V are not shown here, because there are only a very minor changes in the profiles up to 1.02 V. At 1.07 V, the structure factor at all anti-Bragg positions starts to drop below that of a bulk-terminated crystal, indicating an increased roughness of the surface. Interestingly, the minimum at (2 2 1) drops slightly lower than the minimum at

(2 2 3), while (2 2 5) is again lower than what would be expected from the increased Debye-Waller factor alone. A similar behaviour can be seen at (2 0 1), (2 0 3) and (2 0 5), but here the relationship between the relative heights of the minima is inverted. This feature can be explained by a modulation of the CTRs by an oscillation with a periodicity of about $\Delta L \approx 4$. One possible cause for that is a change in the interplanar distance of about half of the bulk lattice spacing. To exemplifying the differences in the CTRs caused by different surface oxide structures, we discuss fits of the CTR data at 1.12 V by selected models. As already discussed in the previous section, variation of the interplanar distances of the two top Pt layers is necessary to adequately describe an undisturbed Pt(100) surface in the double layer region. After oxidation, the increased roughness can be described by at least one additional partially occupied Pt layer at the surface, representing the Pt atoms in the newly formed oxide. The dissolution of Pt in the initial stages of oxidation is below $1\,\mu\mathrm{ML}$, as can be calculated from Fig. 1 with conversion factors of $1.30 \cdot 10^{15}$ and $1.49 \cdot 10^{15}$ $\mathrm{atoms/cm^2}$ for surface atomic densities of Pt(100) and Pt(111), respectively. This very small loss in the number of Pt surface atoms is far below the detection limit of SXRD. We therefore assume in our models that the overall number of Pt atoms on the surface is conserved and that all extracted Pt atoms are bound in the formed Pt surface oxide. In total, four possible lateral locations of the Pt_{ex} atoms were considered in the modelling, which are illustrated in Supplementary Figure 4. In the models, the Pt_{ex} were placed either in atop (1), hollow (3) or bridge (4) sites. Furthermore, an oxide structure was considered where the Pt_{ex} form a layer without long-range order, i.e. are bound in an amorphous oxide (2). The vertical position of the extracted atoms was a free parameter of the fit. Best fits of the CTRs at 1.12 V using these models are shown in Supplementary Figure 4 and the



Supplementary Figure 4. CTR data of the oxide structure at 1.12 V and CTR fits with different in-plane locations of the Pt_{ex} in the oxide structure. A graphic illustration at the top right corner shows the lateral position of the Pt_{ex} atom in the different oxide models. The fits and the diffraction rods in the graph are spaced vertically with an offset factor of 10.

corresponding fit parameters and reduced χ_r^2 are given in Supplementary Table 3. Models 1,2 and 3 show systematic deviations from the data, which are most prominent at (2 2 1), where the shift of the minimum towards lower L is only described well by the bridge site model (4). Similarly, the shift of the minimum of the CTR at (2 0 1) towards higher L is also only well represented by a fit using this oxide model. Also the lowest value of χ_r^2 is obtained using a fit of model 4. Furthermore, we assessed the influence of surface oxygen species on the CTR fits. A comparison of CTR fits with a model containing only the Pt atoms and with an additional monolayer of O_{ads} in bridge sites is shown in Supplementary Figure 5 for 0.95 V, 1.07 V, 1.12 V and 1.17 V. Similarly to the fit of the smooth surface at 0.95 V, inclusion of O_{ads} only leads to a small improvement of the fit, which is

$\mathbf{Pt}_{ex}$ **location**	**atop (1)**	**disordered (2)**	**hollow (3)**	**bridge (4)**
$\boldsymbol{\theta_{ex}}$/ML	0.415 ± 0.009	0.394 ± 0.008	0.1948 ± 0.0023	0.404 ± 0.007
$\boldsymbol{d_{ex}}$/Å	2.22 ± 0.04		1.9395 ± 0.0030	1.409 ± 0.016
$\boldsymbol{d_{12}}$/Å	1.9425 ± 0.0013	1.9428 ± 0.0013	1.9574 ± 0.0012	1.9439 ± 0.0011
$\boldsymbol{d_{23}}$/Å	1.9707 ± 0.0008	1.9703 ± 0.0007	1.9755 ± 0.0007	1.9701 ± 0.0006
$(\boldsymbol{\Delta r_{ex}})_{\parallel}$/Å	0.796 ± 0.030		0.07 ± 0.06	0.491 ± 0.013
$(\boldsymbol{\Delta r_1})_{\parallel}$/Å	0.087 ± 0.011	0.097 ± 0.009	0.075 ± 0.014	0.093 ± 0.008
$(\boldsymbol{\Delta r_2})_{\parallel}$/Å	0.090 ± 0.004	0.089 ± 0.004	0.074 ± 0.005	0.086 ± 0.004
$(\boldsymbol{\Delta r_{ex}})_{\perp}$/Å	0.24 ± 0.04		0.074 ± 0.008	0.242 ± 0.019
$(\boldsymbol{\Delta r_1})_{\perp}$/Å	0.0965 ± 0.0021	0.1011 ± 0.0019	0.0953 ± 0.0019	0.0973 ± 0.0017
$(\boldsymbol{\Delta r_2})_{\perp}$/Å	0.0947 ± 0.0010	0.0954 ± 0.0010	0.0937 ± 0.0009	0.0955 ± 0.0009
$\boldsymbol{\chi_r^2}$	4.285	4.443	3.51	3.229

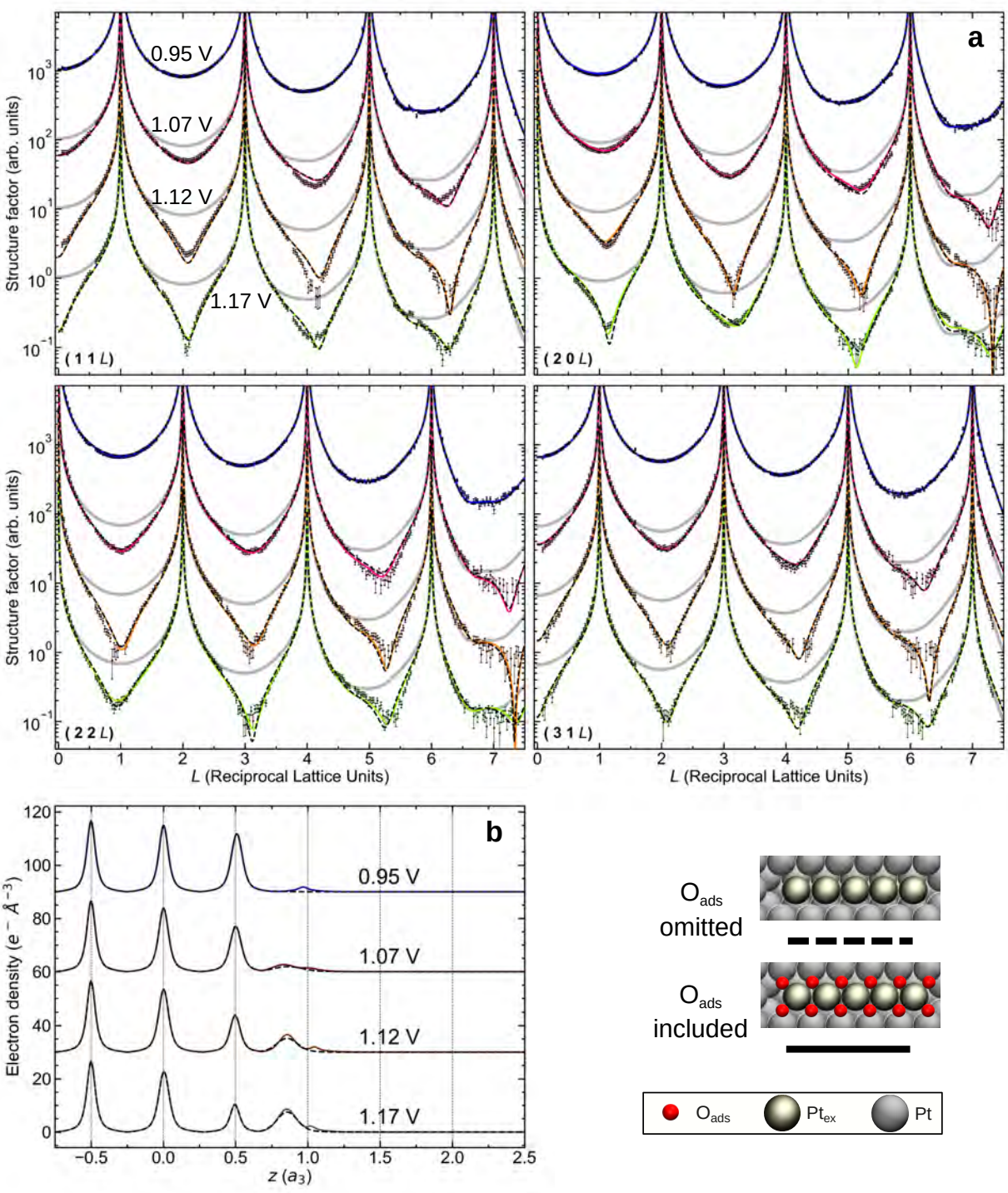
Supplementary Table 3. Structural parameters of the 4 considered oxide structures obtained by fits of the CTRs at E = 1.12 V, which are shown in Supplementary Figure 4. Errors are estimated from the diagonals of the covariance matrix.

insufficient for an exact determination of the lateral O_{ads} locations. Nevertheless, a monolayer of O_{ads} was included in the model employed for the data in Fig. 2 as surface oxygen species obviously are present in the oxide. The lateral location of the O_{ads} was set to the bridge site configuration, predicted by the DFT calculations. Vertical spacing and coverage of the Pt_{ex} obtained from the fits with and without O_{ads} are given in Supplementary Table 4. In both cases, coverage and position of the Pt_{ex} are very similar. For the structural parameters of the Pt layers underneath the two models result in even smaller differences of 1-2%. In addition, we also performed fits (with and without O_{ads}) in which also the third Pt layer was allowed to relax. These resulted in even lower χ_r^2 values, but the Pt_{ex} vertical position and coverage remained very similar.

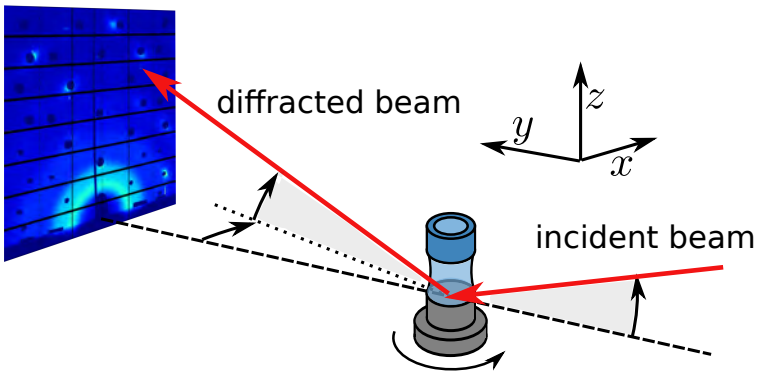
The above results demonstrate clearly that the location of the Pt_{ex} atoms in the surface oxide phase, which is the main result of the structural analysis and the basis of the comparison with the DFT results, is a robust result and does not depend on the specific choice of the model employed in the CTR analysis.

1.07 V	3 relaxed layers		4 relaxed layers	
	O_{ads} included	O_{ads} omitted	O_{ads} included	O_{ads} omitted
$\boldsymbol{\theta_{ex}}$/ML	0.213 ± 0.008	0.208 ± 0.008	0.230 ± 0.006	0.223 ± 0.006
$\boldsymbol{d_{ex}}$/Å	1.29 ± 0.04	1.41 ± 0.05	1.307 ± 0.030	1.40 ± 0.04
$\boldsymbol{\chi_r^2}$	1.98	2.07	1.24	1.32
1.12 V	3 relaxed layers		4 relaxed layers	
	O_{ads} included	O_{ads} omitted	O_{ads} included	O_{ads} omitted
$\boldsymbol{\theta_{ex}}$/ML	0.405 ± 0.007	0.404 ± 0.007	0.320 ± 0.007	0.301 ± 0.007
$\boldsymbol{d_{ex}}$/Å	1.409 ± 0.014	1.409 ± 0.016	1.297 ± 0.023	1.322 ± 0.010
$\boldsymbol{\chi_r^2}$	3.21	3.23	1.84	1.75
1.17 V	3 relaxed layers		4 relaxed layers	
	O_{ads} included	O_{ads} omitted	O_{ads} included	O_{ads} omitted
$\boldsymbol{\theta_{ex}}$/ML	0.5836 ± 0.0008	0.577 ± 0.006	0.5347 ± 0.0012	0.5193 ± 0.0010
$\boldsymbol{d_{ex}}$/Å	1.4070 ± 0.0021	1.417 ± 0.012	1.328 ± 0.004	1.3385 ± 0.0029
$\boldsymbol{\chi_r^2}$	3.18	3.52	2.00	2.20

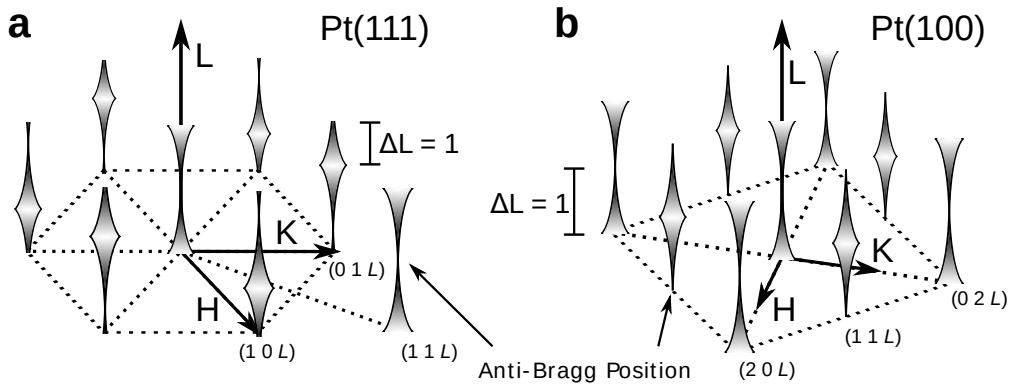
Supplementary Table 4. Coverage θ_{ex} and vertical position d_{ex} of the extracted Pt atoms obtained from CTR fits of the oxide structure at 1.07 V, 1.12 V and 1.17 V using 4 different oxide models. This allows an estimation of the systematic error due to the choice of the surface oxide model.



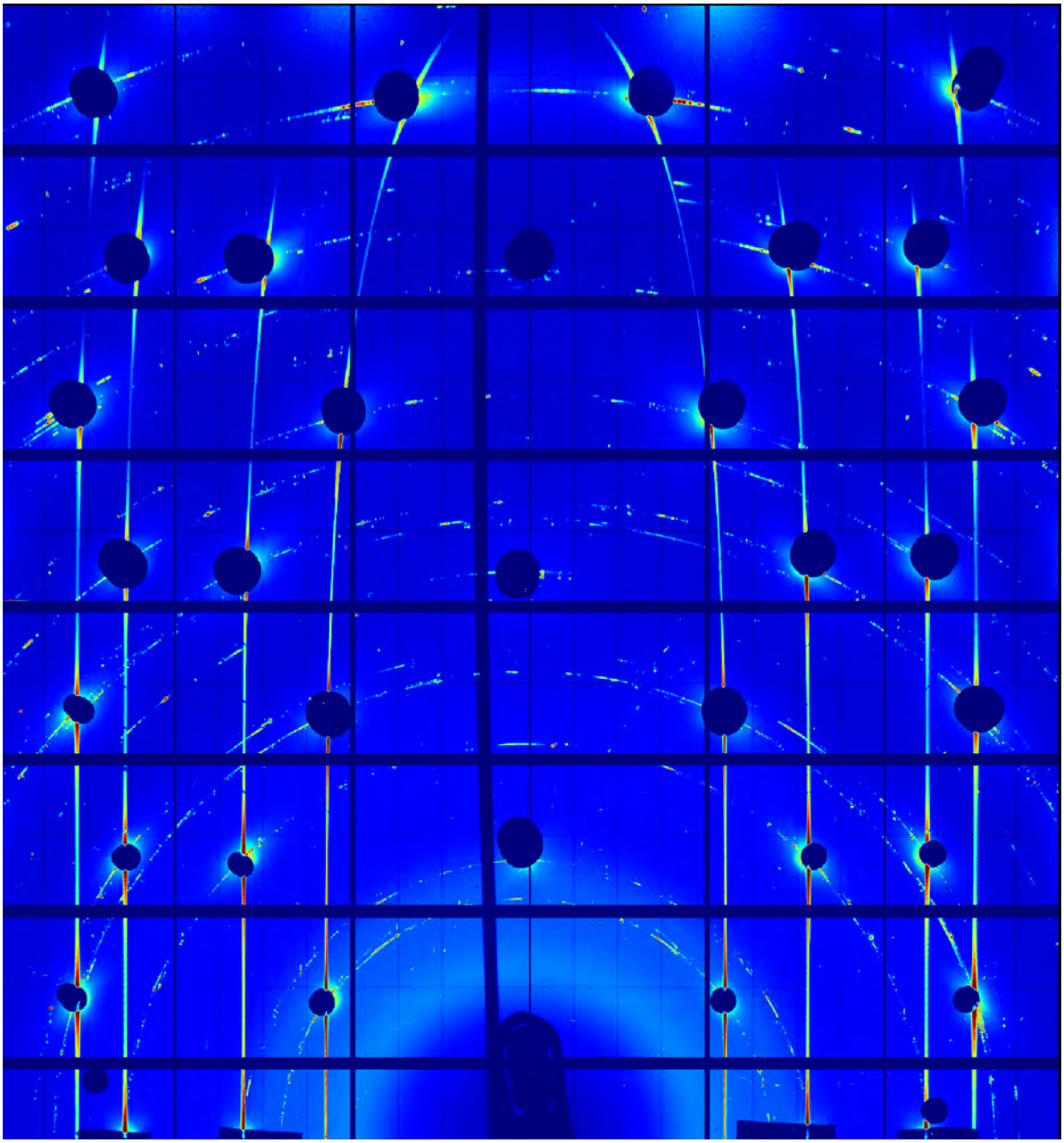
Supplementary Figure 5. **(a)**: CTRs and corresponding fits at 0.95 V, and at 3 different potentials in the region of oxide formation using a surface model with adsorbed oxygen (O_{ads}, solid lines) or omitting O_{ads} (dashed lines). The grey line shows the fit of the smooth surface at 0.95 V. **(b)**: Electron density obtained from the CTR fits.



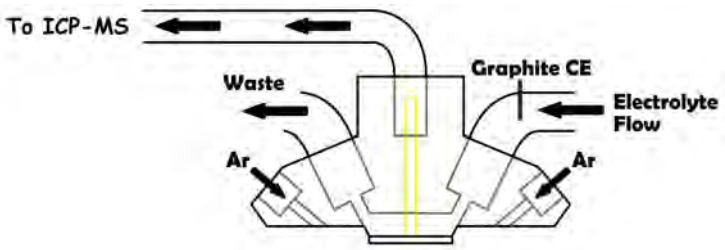
Supplementary Figure 6. Schematic illustration of the diffraction geometry, showing the incident and scattered X-ray beam (red).



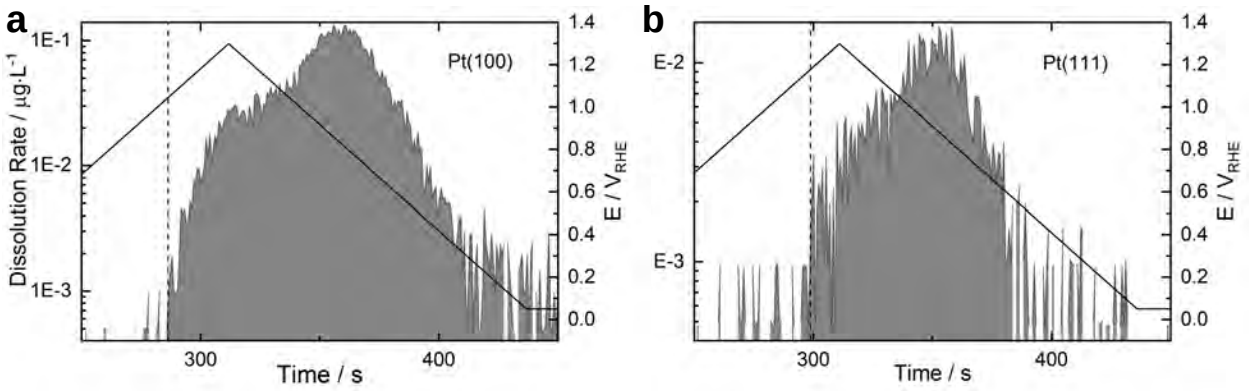
Supplementary Figure 7. Schematic illustration of the reciprocal space geometry for **(a)** Pt(111) and **(b)** Pt(100). The typical intensity distribution along the CTRs is indicated by the widths of the rods.



Supplementary Figure 8. Combination of all 2200 detector frames recorded during a reciprocal space mapping of Pt(100) at 0.12 V using HESXRD at ID31. The CTRs appear as vertical lines, which bend towards the center of the image in the upper part of the image due to the curvature of the Ewald sphere. In this representation, some symmetrically equivalent CTRs lie on top of each other. The black horizontal and vertical bars are insensitive parts of the detector; the black circles along the CTRs are beam stops, placed at the positions of Bragg reflections. The image has been normalized using a logarithmic scale.



Supplementary Figure 9. Scheme of CSFC-ICP-MS cell.



Supplementary Figure 10. Estimation of the onset potential of Pt dissolution on Pt(100) **(a)** and Pt(111) **(b)**. A line was drawn from the visible onset of dissolution over the baseline to the corresponding potential (3 repeat experiments for each surface).

$\theta_{\mathbf{O}}$	$\Delta\mathbf{G_O}$ @ Pt(111)	$\Delta\mathbf{G_O}$ @ Pt(100)	ZPE @ Pt(111)	$\mathbf{TS_{vib}}$ @ Pt(111)	ZPE @ Pt(100)	$\mathbf{TS_{vib}}$ @ Pt(100)
0.11	1.19	1.16	0.07	0.04	0.07	0.05
0.22	1.24	1.17	0.14	0.10	0.14	0.11
0.33	1.36	1.24	0.22	0.11	0.21	0.15
0.44	1.49	1.28	0.31	0.14	0.29	0.22
0.56	1.61	1.30	0.39	0.17	0.37	0.23
0.67	1.71	1.45	0.48	0.20	0.45	0.29
0.78	1.91	1.53	0.56	0.23	0.54	0.31
0.89	2.08	1.62	0.62	0.28	0.63	0.35
1.00	2.24	1.68	0.67	0.34	0.71	0.39

Supplementary Table 5. Average adsorption energies of oxygen (in eV/O_{ads}) and zero-point energy (ZPE), and vibrational entropy (TS_{vib}, at T = 298.15 K) corrections in eV for O_{ads} on Pt(111) and Pt(100).

species	ZPE	TS	$\Delta\mathbf{G_{sol}}$
H_2O	0.58	0.67	-
H_2(g)	0.28	0.40	-
$\cdot H_2O$	0.64	0.18	-0.51

Supplementary Table 6. Zero-point energy (ZPE), entropy (TS, at T = 298.15 K) and solvation (G_{sol}) corrections for various fluid-phase and adsorbed species. [3] All values are in eV.

Supplementary References

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